In connection with the below identified patent application, we hereby acknowledge receipt of:

RCE
Amendment
Information Disclosure Statement
Form 1449
References (3)

DN. A01456 Ser. No. 10/686,305 Filed 10-15-03
Certificate of Mailing: ☒ Yes ☐ No
Date Mailed 4-19-07 Initials CPH/jls

FORM 13663 6/94

PTO/SB/30 (04-07)
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Request for Continued Examination (RCE) Transmittal

Address to:
Mail Stop RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Application Number	10/686,305
Filing Date	10/15/2003
First Named Inventor	Peter David Berezuk
Art Unit	1711
Examiner Name	Terressa M. Boykin
Attorney Docket Number	A01456

This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application.
Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application. See Instruction Sheet for RCEs (not to be submitted to the USPTO) on page 2.

1. Submission required under 37 CFR 1.114 Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).

   a. ☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.
      i. ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on ____________
      ii. ☐ Other ____________

   b. ☑ Enclosed
      i. ☑ Amendment/Reply
      ii. ☐ Affidavit(s)/ Declaration(s)
      iii. ☑ Information Disclosure Statement (IDS)
      iv. ☐ Other ____________

2. Miscellaneous

   a. ☐ Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of ________ months. (Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(i) required)
   b. ☐ Other ____________

3. Fees The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed.

   a. ☑ The Director is hereby authorized to charge the following fees, any underpayment of fees, or credit any overpayments, to Deposit Account No. 18-1850. I have enclosed a duplicate copy of this sheet.
      i. ☑ RCE fee required under 37 CFR 1.17(e)
      ii. ☐ Extension of time fee (37 CFR 1.136 and 1.17)
      iii. ☐ Other ____________
   b. ☐ Check in the amount of $ ____________ enclosed
   c. ☐ Payment by credit card (Form PTO-2038 enclosed)

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED

Signature	Carl P. Hemenway	Date	April 19, 2007
Name (Print/Type)	Carl P. Hemenway	Registration No.	51,798

CERTIFICATE OF MAILING OR TRANSMISSION

I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Mail Stop RCE, Commissioner for Patents, P. O. Box 1450, Alexandria, VA 22313-1450 or facsimile transmitted to the U.S. Patent and Trademark Office on the date shown below.

Signature	Janice Soulas		
Name (Print/Type)	Janice Soulas	Date	4-19-07

This collection of information is required by 37 CFR 1.114. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Mail Stop RCE, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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Docket No.: : A01456

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. : 10/686,305
Applicant : Peter David Berezuk
Filed : 10/15/2003
Title : Method for Preparing a Bonded Composite

TC/Art Unit : 1711
Examiner : Terressa M. Boykin

Mail Stop RCE
Commissioner for Patents
PO Box 1450
Alexandria, VA 22313-1450

AMENDMENT

Sir:

In connection with the Request for Continued Examination filed herewith in connection with the above-identified application, Applicants respond as follows.

Amendments to Claims: begin on page 2 of this paper

Remarks/Arguments: begin on page 7 of this paper.

AMENDMENTS TO CLAIMS:

This listing of claims will replace all prior versions, and listings, of claims in the application:

1. (currently amended) A method of preparing a cured bonded composite; wherein said cured bonded composite comprises two or more substrates bonded together with an interposed bonding composition; wherein said method comprises the steps of:
   a) applying onto a first substrate, a prepolymer composition, wherein said prepolymer composition comprises, in weight percent, based on the weight of said prepolymer composition:
      (i) from 15% to 70% of at least one uncurable polyester resin,
      wherein said uncurable polyester resin is the reaction product of reacting one or more hydrocarbon having two or more hydroxyl groups with one or more polycarboxylic acid that is aliphatic, cyclic aliphatic, or aromatic,
      wherein said resin contains fewer curable reactive groups than 0.01 mole/kg of resin,
      wherein said resin has number-average molecular weight of 6,500 or less, and
      wherein said resin has acid value of 2 mg KOH/g of resin or greater; and
      (ii) from 30% to 85% of a least one polymerizable compound;
   b) contacting a second substrate with said prepolymer composition to provide an uncured composite, wherein said prepolymer composition is in contact with said first substrate and said second substrate; and
   c) subjecting said uncured composite to electron beam radiation to provide said cured bonded composite;

   wherein each said polymerizable compound in said prepolymer composition is a monomer or oligomer selected from the group consisting of alkyl esters of (meth)acrylic acid, hydroxyl containing esters of (meth)acrylic acid, ring containing esters of (meth)acrylic acid, esters of (meth)acrylic acid containing ethylene oxide, esters of (meth)acrylic acid containing glycidyl groups, esters of (meth)acrylic acid with polyols, adducts of acrylic compounds with epoxy compounds, adducts of acrylic compounds with phosphate compounds, acrylic oligomers, ethylenically unsaturated compounds other than (meth)acrylate compounds, and mixtures thereof; and

wherein said prepolymer composition is capable of being applied onto a substrate by one or more of roll coating, rod coating, gravure, or Meyer bar, and

wherein said prepolymer composition contains no solvent.

2. (original) The method of claim 1, wherein said polymerizable compound comprises at least one monomer selected from the group consisting of esters of acrylic acid with a polyol, esters of methacrylic acid with a polyol, and mixtures thereof.

3. (original) The method of claim 1, wherein said uncured composite is subjected to said electron beam radiation with a dose of 20 kGy (2 Mrad) to 70 kGy (7 Mrad).

4. (cancelled)

5 (currently amended) A composition useful as an adhesive when cured by electron beam radiation comprising a prepolymer composition, wherein said prepolymer composition comprises, in weight percent, based on the weight of said prepolymer composition:

(i) from 15% to 70% of at least one uncurable polyester resin,

wherein said uncurable polyester resin is the reaction product of reacting one or more hydrocarbon having two or more hydroxyl groups with one or more polycarboxylic acid that is aliphatic, cyclic aliphatic, or aromatic,

wherein said resin contains fewer curable reactive groups than 0.01 mole/kg of resin, wherein said resin has number-average molecular weight of 6,500 or less, and

wherein said resin has acid value of 2 mg KOH/g of resin or greater; and

(ii) from 30% to 85% of a least one polymerizable compound;

wherein each said polymerizable compound in said prepolymer composition is a monomer or oligomer selected from the group consisting of alkyl esters of (meth)acrylic acid, hydroxyl containing esters of (meth)acrylic acid, ring containing esters of (meth)acrylic acid, esters of (meth)acrylic acid containing ethylene oxide, esters of (meth)acrylic acid containing glycidyl groups, esters of (meth)acrylic acid with polyols, adducts of acrylic compounds with epoxy compounds, adducts of acrylic compounds with phosphate compounds, acrylic oligomers, ethylenically unsaturated compounds other than (meth)acrylate compounds, and mixtures thereof;

wherein said prepolymer composition is a uniform solution; and

wherein said prepolymer composition is capable of being applied onto a substrate by one or more of roll coating, rod coating, gravure, or Meyer bar, and

wherein said prepolymer composition contains no solvent.

6. (original) The composition of claim 5, wherein said polymerizable compound comprises at least one monomer selected from the group consisting of esters of acrylic acid with a polyol, esters of methacrylic acid with a polyol, and mixtures thereof.

7. - 8. (cancelled)

9. (previously presented) The composition of claim 5, wherein said prepolymer composition contains no effective amount of photoinitiator.

10. (previously presented) The composition of claim 5, wherein said prepolymer composition has viscosity of 1.0 to 5.0 Pa*s.

11. (previously presented) The method of claim 1, wherein said prepolymer composition contains no effective amount of photoinitiator.

12. (previously presented) The method of claim 1, wherein said prepolymer composition has viscosity of 1.0 to 5.0 Pa*s.

13. (previously presented) The method of claim 1, wherein said step of applying is performed by roll coating, rod coating, gravure, or Meyer bar.

14. (new) The method of claim 2, wherein said polyol is selected from the group consisting of ethylene glycol, propylene glycol, glycerol, pentaerythritol, trimethylolpropane, hexane diols, butane diols, polyethylene glycol, polypropylene glycol, ethylene-propylene copolymer glycol, ethoxylated pentaerythritol, propoxylated pentaerythritol, ethoxylated trimethylolpropane, propoxylated trimethylolpropane, ethoxylated hexane diols, propoxylated hexane diols, and mixtures thereof.

15. (new) The method of claim 1, wherein all of said polymerizable compounds are selected from the group consisting of monomers, oligomers made by reacting one or more acrylic monomers with each other, and mixtures thereof.

16. (new) The method of claim 15, wherein all of said polymerizable compounds are monomers.

17. (new) The composition of claim 6, wherein said polyol is selected from the group consisting of ethylene glycol, propylene glycol, glycerol, pentaerythritol, trimethylolpropane, hexane diols, butane diols, polyethylene glycol, polypropylene glycol, ethylene-propylene copolymer glycol, ethoxylated pentaerythritol, propoxylated pentaerythritol, ethoxylated trimethylolpropane, propoxylated

trimethylolpropane, ethoxylated hexane diols, propoxylated hexane diols, and mixtures thereof.

18. (new) The composition of claim 5, wherein all of said polymerizable compounds are selected from the group consisting of monomers, oligomers made by reacting one or more acrylic monomers with each other, and mixtures thereof.

19. (new) The composition of claim 18, wherein all of said polymerizable compounds are monomers.

REMARKS/ARGUMENTS

Claims 1-3, 5-6, and 9-19 remain in this application. Claims 4, 7, and 8 are cancelled, without prejudice. Claims 14 - 19 are new.

Amendments: Lack of New Matter

Applicant submits that the forgoing claim amendments do not introduce new matter into the present application. The features recited in the forgoing amendments are found in the present specification as follows.

Claims 1 and 5: Polyester resin with number-average molecular weight of 6,500 or less is on p. 6, lines 3-10.

Claims 14 and 17: List of polyols on p. 8, line 29 to p. 9, line 5.

Claims 15 and 18: Preference for monomers and oligomers, on p. 10, lines 15-17; and preference for oligomers to be acrylic, p. 9, line 30 to p. 10, line 2.

Claims 16 and 19: Preference for monomers, on p. 10, lines 15-17.

Applicants respectfully request the Examiner to allow claims 1-3, 5-6, and 9- 19 at this time. If, however, there remain any open issues which the Examiner believes can be resolved by a telephone call, the Examiner is cordially invited to contact the undersigned agent.

A fee of $790 is authorized herewith for the Request for Continued Examination submitted herewith. No additional fees are believed to be due in connection with the submission of this amendment; however, if any such fees, including petition or extension fees, are due, the Commissioner is hereby authorized to charge them, as well as to credit any overpayments, to Deposit Account No. 18-1850.

Comment on Accompanying References

Accompanying this Amendment is an Information Disclosure Statement and three Japanese references, with an English translation of each. Applicants wish to make note of JP 57-008273; in a previous IDS, Applicants submitted a Derwent abstract of this reference, and Applicants consider the English translation of JP 57-008273 enclosed herewith to be a more accurate presentation of the subject matter of JP 57-008273 than the Derwent abstract that was previously submitted.

Respectfully Submitted,

Carl P. Hemenway

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Rohm and Haas Company
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Date: April 19, 2007

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Atty Docket No.: A01456

In re Application of:

Peter David Berezuk

Application No.: 10/686,305

Filed: October 15, 2003

For: METHOD FOR PREPARING A BONDED COMPOSITE

Group Art Unit: 1711

Examiner: Terressa M. Boykin

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

INFORMATION DISCLOSURE STATEMENT

Sir:

In accordance with Applicant(s)' duty of disclosure under 37 CFR §§ 1.97 to 1.98, Applicant(s) submit(s) herewith substitute for form 1449/PTO "Information Disclosure Statement by Applicant". Inclusion of a document in this Information Disclosure Statement or on its attached form PTO-1449 is not intended to constitute an admission that any document so disclosed is "prior art" with respect to the present invention unless specifically so stated herein.

The filing of the Information Disclosure Statement shall not be construed to mean that a search has been made, or that no other material information, as defined in 37 CFR 1.56(a), exists.

As per the OG, August 05, 2003, waiver of Rule 37 CFR 1.98 (a) (2) (i), Applicant (s) have not submitted any copies of U.S. Patents and Published Applications since this application was filed after June 30, 2003.

The Examiner is requested to review the references cited herein and to make the references cited of record in the present application.

Respectfully submitted,

Carl P. Hemenway

Carl P. Hemenway
Attorney for Applicant(s)
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Date: April 19, 2007

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PTO/SB/08A (09-06)
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Substitute for form 1449/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet 1 of 1

Complete if Known

Application Number	10/686,305
Filing Date	October 15, 2003
First Named Inventor	Peter David Berezuk
Art Unit	1711
Examiner Name	Terressa M. Boykin
Attorney Docket Number	A01456

U. S. PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US-			
		US-			
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FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3]-Number[4]-Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages Or Relevant Figures Appear	T[6]
		JP 57-8273	01-16-1982	DAI NIPPON PRINTING		✓
		JP 8-81653	03-26-1996	KANSAI PAINT CO., LTD.		✓
		JP 2000-80343	03-21-2000	KANSAI PAINT CO., LTD.		✓
						☐
						☐
						☐

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. [1] Applicant's unique citation designation number (optional). [2] See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. [3] Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). [4] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [5] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [6] Applicant is to place a check mark here if English language Translation is attached.

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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TRANSLATED FROM JAPANESE BY ACCURAPID – THE LANGUAGE SERVICE

(19) Japanese Patent Office (JP)

Publication of Laid Open Patent Application (A)

(11) Patent Application Disclosure
S57-8273

(43) Publication Date: January 16, 1982

(51) Int. Cl.³	ID Code	(52) Japan Classification	Administration No.
C 09 J 3/14	CEM	7016-4J	
// C 08 F 299/04		7919-4J	

Request for Examination: Not Requested　Number of Inventions: 1　Total pages: 4

(54) Adhesive Composition for Laminate

(21) Filing No.: S55-83086

(22) Filing Date: June 19, 1980

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(74) Agent ONISHI, Atsumi

Specification

1. Title of the Invention　Adhesive Composition for Laminate

2. Extent of Patent Claims

What Is Claimed Is:

An adhesive composition for an electron beam hardening laminate consisting of a compound with an ethylenic unsaturated bond and a linear saturated polyester resin composing between 5 and 60% by weight of the total.

3. DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to an adhesive composition for an electron beam hardening laminate. In further detail, the present invention relates to an adhesive composition for an electron beam hardening laminate that can provide an adhesive layer that is flexible and has excellent adhesive force.

Various types of lamination films are being used, primarily as packaging materials. Methods to produce these lamination films are already known, including dry lamination, extrusion lamination, and wet lamination, and the like. Adhesives are used for this lamination, and for instance polyurethane adhesive, polyacrylic ester adhesive, epoxy resin adhesive, vinyl chloride/vinyl acetate copolymer adhesive, and isocyanate adhesive, and the like, are used. However, these adhesives are dissolved and used in organic solvents such as ethyl acetate, methyl ethyl ketone, toluene, xylene, or hexane, or the like, so during the adhesion operation or during drying, large quantities of organic solvents are dispersed into the atmosphere, which not only has the problem of significantly degrading the working environment, but also is very uneconomical from a thermal perspective. Furthermore, because trace amounts of organic solvent cannot be prevented from remaining between the laminate films, the use in applications where odors are undesirable or in packaging for materials where odors can easily be absorbed, and even if used, product value will be degraded by the odor of the residual solvent. Furthermore, the use of large amounts of organic solvent is not preferable from the viewpoint of consuming natural resources.

In contrast, an electron beam hardening adhesion method which uses a solvent-free adhesive not only eliminates the problems with a conventional laminate method which uses a solvent diluted adhesive as described above, but also provides advantages such as the line speed can be increased so productivity is increased, a long drying furnace is not necessary, equipment floor space is reduced, production control is simplified with momentary start up and stopping, and material losses during start up and stopping are minimized, so broad use is anticipated, primarily for lamination films using packaging material. However, adhesives which use this method are expected to harden completely, so there are disadvantages in that the flexibility of the hardened layer obtained is low, and the adhesive strength is still insufficient.

The present invention is a new composition that improves the flexibility and adhesion of adhesives for conventional electron beam hardening laminates, and consists of a compound with an ethylenic unsaturated bond and a linear saturated polyester resin composing between 5 and 60% by weight of the total. If the amount is less than 5%, the flexibility of the hardened adhesive will be poor, but if the amount exceeds 60%, the viscosity of the composition will be high, and the painting process will be difficult.

The linear saturated polyester resin of the present invention consists of a diacid base residue and a diol residue, and resin which has a molecular weight between 10,000 and 30,000, a limiting viscosity between 0.5 and 1.0, and a glass transition temperature of 10°C or lower is suitable for the present invention. Examples of the dibasic acid component include aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, 1, 2-bis(P-carboxyphenoxy) ethane, 2, 2-bis(P-carboxyphenyl) propane, and aliphatic carboxylic acids such as dicarboxylic acid, succinic acid, adipic acid, and subacic acid and the like. Examples of the diol component include aliphatic, aromatic, and alicyclic diols such as ethylene glycol, propylene glycol, tetramethylene glycol, pentamethylene glycol, 2, 2-dimethyltrimethylene glycol, hexamethylene glycol, P-xylene glycol, and cyclohexane dimethanol. Furthermore, the diol component may also be a block copolymer polyester which has as polymer components aliphatic polyester glycols such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polyethers such as the copolymers of ethylene oxide and propylene oxide, polyneopentyl acetate, and polyneopentyl adipate, and the like.

Examples of the compound with an ethylenic unsaturated bond of the present invention include polyester (meth)acrylate, polyurethane (meth)acrylate, polyepoxy (meth)acrylate, polyether (meth)acrylate, and other prepolymers; styrene, α-styrene, vinyl acetate, and other olefinic monomers; methyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, methoxyethyl acrylate, butoxyethyl acrylate, butyl acrylate, methoxybutyl acrylate, cyanoacrylate, cyanoethyl acrylate, phenyl acrylate, and other acrylate esters; methyl methacrylate, propyl methacrylate, methoxyethyl methacrylate, ethoxymethyl methacrylate, phenyl methacrylate, ethyl methacrylate, lauryl methacrylate, and other methacrylate esters; acrylamide, methacrylamide, N-N-dimethylacrylamide, N-N diisopropylamide, N,N-didecylacrylamide, N,N-dimethyl methacrylamide, N,N- diethylmethacrylamide and other unsaturated carboxylamide and derivatives thereof; 2-(N,N-dimethylamine) ethyl acrylate, 2-(N,N-dimethylamino) ethyl acrylate, 2-(N,N-dibenzylamino) ethyl acrylate, (N,N-dimethylamino) methyl methacrylate, 2-(N,N-diethylamino) propyl acrylate and other similar compounds; ethylene glycol diacrylate, propylene glycol diacrylate, neopentyl glycol diacrylate, 1,6-hexanediol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, dipropylene glycol diacrylate, ethylene glycol dimethacrylate, propylene glycol dimethacrylate, diethylene glycol dimethacrylate, and other by functional monomers, trimethylol propane triacrylate and other trifunctional monomers or similar compounds, and these compounds may be used individually or two or more may be used as a blend.

The adhesive composition of the present invention is prepared by blending and kneading using standard methods while heating the aforementioned components if necessary to make an adhesive with a viscosity in a range between 100 and 800 cp. Note, if necessary, plasticizers or polymerization inhibitors, or the like, may be added to the adhesive composition of the present invention.

The composition of the present invention is used for adhesion between similar or different types of films such as paper, plastic, or metal, and the like. Examples of plastic films include stretch or non-stretch films of various resins such as cellophane, low density, medium density, or high density polyethylene, polypropylene, polyethylene terephthalate, polyamide, polycarbonate, polyacetate, polyvinylchloride, polyvinylidenechloride, polyvinyl alcohol, ethylene-vinyl alcohol copolymer, ethylene-vinyl acetate copolymer, ethylene-α- olefin copolymer, ionomer resin, and poly-1, 2-butadiene, as well as metal vapor deposition films such as aluminum, or the like, or paint films such as polyvinylidene chloride, vinyl chloride-vinyl acetate copolymer, or hardened [illegible] formed on these plastic films. If necessary, these films may be surfaced treated with a Corona treatment, or the like, prior to application of the adhesive.

In order to obtain a laminate film using the adhesive composition of the present invention, all or any part of a base material film is coated with the composition of the present invention at a rate of between 0.2 and 20 g/m^2, preferably between 0.4 and 10 g/m^2, using a gravure coating method, roll coating method, or the flexo-reverse method, or the like, and then applying a different film (either the same or a different type than the base material film), or extruding another film base material and then laminating multiple layers together, after which the adhesive composition is hardened using electron beam irradiation. Laminate films with three or more layers can be obtained by a method where the aforementioned method is repeated using a multiple layer film as a base material, or a method where 3 or more films to which the adhesive of the present invention has been applied are overlaided and multiple layers of adhesive are hardened by a single electron beam irradiation.

The electron beam used to harden the adhesive is an electronic beam with energy in the range between 50 to 1000 KeV, preferably between 100 and 300 KeV, irradiated from one of various types of electron beam accelerators including a Cockcroft-Walton accelerator, Van de Graaff accelerator, resonance transformer accelerator, insulated core transformer accelerator, linear accelerator, dynamitron accelerator, or high-frequency accelerator, or the like. In order to irradiate the adhesive layer with an electron beam, either a method where a spot beam travels at high speed or a method where a continuous curtain shaped beam is continuously irradiated from a linear filament is used. Normally surface irradiation is performed by continuously moving the object that is subject to irradiation.

The adhesive composition of the present invention is basically a solvent free composition. Therefore, a laminate film made odor-free by completely hardening using electron beam irradiation in this manner can be extremely useful as a packaging material for various types of food and drugs.

The present invention will be more specifically described below using the following embodiments.

Embodiment 1

Pyron 300 (product of Toyo Boshoku)(linear saturated polyester)	30% by weight
Elestra XRA/234 (product of Mitsui Toatsu) (polyester acrylate)	30% by weight
2-hydroxyethyl acrylate	40% by weight

The aforementioned formulation was heated to 125°C to completely dissolve the linear saturated polyester which was a solid, in order to obtain a uniform liquid composition with a viscosity of 700 cp (measured at 25°C).

This composition was applied to a 12 µm thick biaxially elongated polyethylene terephthalate film which had been corona treated, at a rate of 40 g/m^2 using a gravure roller, and a 50 µm thick polyethylene film which had been corona treated similar to as described above was overlaid. This combined film (width 450 mm) was rolled at a rate of 60 m/minute in a nitrogen environment while a 150 keV, 5 mA curtain-shaped electron beam was irradiated from the biaxially elongated polyethylene terephthalate film side at an intensity of 1.0 Mrad from a low energy electron beam accelerator (product of Energy Science, Electrocurtain CB20d50/30), in order to harden the adhesive. The adhesive strength (tensile speed 300 mm/min, tensile angle T shaped) of the laminate film obtained was 830 g/15 mm.

Furthermore, a 60 µm polypropylene film was used in place of the polyethylene film of the aforementioned embodiment, and when a test was performed using the same adhesive, the adhesive strength obtained was 760 g/15 mm.

Embodiment 2

Pyron 300 (product of Toyo Boshoku)(linear saturated polyester)	45% by weight
Aronix 6100 (product of Toa Gohsei) (oligoester acrylate)	30% by weight
2- hydroxyethyl acrylate	25% by weight

The above formulation was heated to 125°C to completely dissolve the linear saturated polyester which was a solid, in order to obtain a uniform composition with a viscosity of 580 cp (measured at 25°C).

The same adhesion test as Embodiment 1 was performed using this composition. The adhesive strength of the laminate film obtained was 810 g/15 mm between a biaxially elongated polyethylene terephthalate film and a polyethylene film, and was 790 g/15 mm between a biaxially elongated polyethylene terephthalate film and a polypropylene film.

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Procedural Corrections

August 8, 1980

Patent Office Commissioner KAWAHARA, Yoshio

1. Presentation of Case
   1980 No. 83,086

2. Title of the Invention
   Adhesive Composition for Laminate

3. Revisor

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7. Subject of Revision
   Section of "Detailed Description of the Invention" in the Specification

8. Content of Revisions

(1) A "," was deleted in line 5 of page 4 of the specification.

(2) [Japanese spelling correction] was made on the 2nd line from the bottom of page 8.

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(54) TITLE OF THE INVENTION

Manufacturing Method for a Metal Plate Laminated with Film Having an Ink Layer

(57) ABSTRACT

PURPOSE

To obtain a plastic film-laminated metal plate with an ink layer which has excellent adhesion between a transparent plastic film, ink, and metal plate, excellent processing properties when used to make cans, and which has excellent surface finish and retort resistance properties, and the like.

CONSTITUTION

Laminate a metal plate with an electron beam-hardening adhesive layer having between 0.5 and 250 weight parts of a stress-relaxing agent in 100 weight parts of a resin composition formulated with between 2 and 200 weight parts of polyester oligomer with polymeric unsaturated double bonds in 100 weight parts of polyester resin, an electron beam-hardening ink layer containing a colorant and a resin composition formulated with between 2 and 200 weight parts of oligomer polyester with polymeric unsaturated double bonds in 100 weight parts of polyester resin, and a polyester film, and said adhesive layer and said ink layer are hardened by irradiating with an electron beam.

[Claims]

What Is Claimed Is:

Claim 1

A manufacturing method for a plastic film-laminated metal plate with an ink layer in which an adhesive layer, ink layer, and transparent plastic film are successively overlaid on a metal plate, wherein:

the adhesive layer is consisting of an electron beam-hardening adhesive containing between 0.5 and 250 weight parts of stress-relaxing agent and 100 weight parts of a resin composition formulated to have between 2 and 200 weight parts of a polyester oligomer with an arithmetic mean molecular weight of between 300 and 5000 having between 0.3 and 5.0 mole/kg of molecules with polymeric unsaturated double bonds and 100 weight parts of polyester resin with an arithmetic mean molecular weight of between 7000 and 40,000;

the ink layer consisting of an electron beam-hardening ink containing a colorant and a resin composition formulated to have between 2 and 200 weight parts of polyester oligomer with an arithmetic mean molecular weight between 300 and 5000 having between 0.3 and 5.0 mol/kg of molecules with polymeric unsaturated double bonds and 100 weight parts of polyester resin with an arithmetic mean molecular weight of between 7000 and 40,000; and the electron beam-hardening adhesive and the beam-hardening ink, and the like, are hardened by irradiating with an electron beam through the laminated transparent plastic film.

Claim 2

The manufacturing method according to Claim 1, wherein the transparent plastic film is a polyester film.

Claim 3

The manufacturing method according to Claim 1 or Claim 2, wherein the metal plate which is laminated with a film having an ink layer is a film-laminated metal plate for making cans.

DETAILED DESCRIPTION OF THE INVENTION

[0001] INDUSTRIAL FIELD OF APPLICATION

Present invention relates to a metal plate which is laminated with an electron beam-hardening adhesive, an electron beam-hardening ink, and a transparent plastic film.

[0002] BACKGROUND TECHNOLOGY AND PROBLEMS THEREOF TO BE RESOLVED

Conventionally, metal plate which has been laminated with a transparent plastic film with an ink layer which is used for cans for beverages and cans for food (hereinafter referred to as "film-laminated metal plate") normally consist of a metal plate overlaid with a transparent plastic film such as a polyester film with an ink layer using an adhesive (for instance, refer to Japanese Unexamined Patent Application H3-87249, and the like).

[0003] The manufacturing method for conventional film-laminated metal plate for instance consists of (1) a step of printing ink on a polyester film (hereinafter referred to as "PET film") which is the transparent plastic film, drying, applying an adhesive thereon, and then drying until tack-free (normally at approximately 50°C to 150°C for several seconds); or (2) a step of hardening by heating (normally at approximately 180°C for 0.5 seconds) and compressing a PET film onto which ink and adhesive have been applied, onto a metal plate.

[0004] The aforementioned conventional manufacturing method has the following problems.

1. In order to meet conditions for manufacturing film-laminated metal plate using a high-speed production line necessary for large volume production, the after bake oven must be lengthened and this equipment is large so the equipment expense will increase and more plant space will be required.

2. With a conventional manufacturing method, if the lamination speed exceeds 150 m/min, or if the lamination temperature is below 180°C, areas without sufficient adhesion (insufficient hardening) will appear, and there will be variations in appearance.

3. A can for beverages or a can for food manufactured from film-laminated metal plate obtained by a conventional method has poor processing properties (necking process, flanging process, beading process, and the like) and because of the heat from baking (maximum temperature between 230°C and 240°C for 90 seconds or between 240°C and 280°C for between 7 and 20 seconds) the side seam paint and the heat of welding at the can body seam line in the area of the weld may have whitening or blistering occur after retort processing, a pattern similar to water spots may appear on the surface of the PET film, and surface finish will be poor because of reduced gloss, and the like.

[0005] In order to resolve the aforementioned problems, the present inventors have previously proposed in Japanese Unexamined Patent Application H6-192637 a method for obtaining a film-laminated metal plate using an electron beam hardened adhesive as the adhesive, and after overlaying a polyester film onto a metal plate using electron beam-hardening adhesive, an electron beam is irradiated through the polyester film in order to harden the adhesive.

[0006] These problems could be resolved using the method according to this proposal, but normally a lacquer-type gravure ink is used as the ink, so there were problems with poor adhesion in the processing regions, and whitening and blistering readily occurring in the forming regions because of the retort process.

[0007] With the foregoing in view, an object of the present invention is to provide a film-laminated metal plate with excellent adhesion between the transparent plastic film, ink, and metal plate, and having superior performance in such areas as processability when used to make cans, ability to withstand retorting not only in flat regions but also in formed regions, and superior surface finish when compared to conventional products, without the need for large equipment and space by laminating at high speed and low temperature using electron beam hardening of the ink and adhesive.

[0008] MEANS FOR RESOLVING PROBLEMS

As a result of diligent research to resolve the aforementioned problems, the present inventors have discovered that the aforementioned objectives can be achieved by using electron beam-hardening materials of a specific composition for the adhesive and ink of the film-laminated metal plate, and then hardening by electron beam, and have thus achieved the present invention.

[0009] In other words, the present invention provides:

1. A manufacturing method for a plastic film-laminated metal plate with an ink layer wherein an adhesive layer, ink layer, and transparent plastic film are successively overlaid on a metal plate, wherein:

the adhesive layer is consisting of an electron beam-hardening adhesive containing between 0.5 and 250 weight parts of stress-relaxing agent and 100 weight parts of a resin composition formulated to have between 2 and 200 weight parts of a polyester oligomer with an arithmetic mean molecular weight of between 300 and 5000 having between 0.3 and 5.0 mole/kg of molecules with polymeric unsaturated double bonds and 100 weight parts of polyester resin with an arithmetic mean molecular weight of between 7000 and 40,000;

the ink layer is consisting of an electron beam-hardening ink containing a colorant and a resin composition formulated to have between 2 and 200 weight parts of polyester oligomer with an arithmetic mean molecular weight between 300 and 5000 having between 0.3 and 5.0 mol/kg of molecules with polymeric unsaturated double bonds and 100 weight parts of polyester resin with an arithmetic mean molecular weight of between 7000 and 40,000; and the electron beam-hardening adhesive, and the like, and beam-hardening ink are hardened by irradiating with an electron beam through the laminated transparent plastic film.

[0010] Furthermore, the present invention 2 provides the manufacturing method according to item 1 above, wherein the transparent plastic film is a polyester film.

[0011] Moreover, the present invention 3 also provides the manufacturing method according to item 1 or 2 above, wherein the metal plate which is laminated with a film having an ink layer is a film-laminated metal plate for making cans.

[0012] FUNCTION

The present invention will be described below in detail. The electron beam-hardening adhesive of the present invention is comprising between 0.5 and 250 weight parts of a stress-relaxing agent in 100 weight parts of a resin composition formulated to have between 2 and 200 weight parts of polyethylene oligomer (hereinafter referred to as "oligomer") with an arithmetic mean molecular weight between 300 and 5000 and having between 0.3 to 5.0 mol/kg molecules with polymeric unsaturated double bonds in 100 weight parts of polyester resin.

[0013] Based on the objective of the present invention of adhering to metal and plastic film, the first requirement of the polyester resin composition is adhesion, and if the product is to be formed, flexibility will also be required, and furthermore, water resistance, weather resistance, chemical resistance, heat resistance, and the like, will be required in order to provide durability to the adhesive layer of the laminated metal plate.

[0014] The polyester resin used in the present invention is a commonly known thermoplastic resin that is the product of condensation between a polybasic acid and a polyhydric alcohol with an arithmetic mean molecular weight between 7000 and 40,000, preferably between 10000 and 30,000.

[0015] Examples of polybasic acids include aliphatic dibasic acids such as adipic acid, suberic acid, azelaic acid, sebacic acid, decane-1,10-dicarboxylic acid, and the like; alicyclic polybasic acids such as hexahydrophthalic acid, hexahydrotrimellitic acid, tetrahydrophthalic acid, as well as anhydrides thereof; aromatic polybasic acids such as phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid, as well as anhydrides thereof; and other acids such as maleic acid, fumaric acid, itaconic acid, and the like.

[0016] Examples of polyhydric alcohols include ethylene glycol, propylene glycol, diethylene glycol, 1,2-butylene glycol, 1,6-hexanediol, 1,4-cyclohexane dimethanol, neopentyl glycol, polylactonediol, and the like. Polyester resins are manufactured by condensation polymerization of these acid components and alcohol components in a reaction vessel at a temperature between 200°C and 250°C.

[0017] The oligomer component used in combination with the polyester resin is a polyester oligomer with an arithmetic mean molecular weight between 300 and 5,000, preferably between 1000 and 2000, and has between 0.3 and 5.0 mol/kg, preferably between 1.0 and 3.0 mol/kg of molecules with polymeric unsaturated double bonds.

[0018] The polyester type oligomer can be obtained by ester bonding a (meth)acrylic acid to a low molecular weight polyester with hydroxyl groups having an arithmetic mean molecular weight of 5000 or less, and the low molecular weight polyester can be obtained by condensing a polyhydric alcohol with the aforementioned polybasic acid of the polyester resin composition.

[0019] If the arithmetic mean molecular weight of the aforementioned polyester resin is below 7000, there is a tendency towards poor corrosion resistance and water resistance. On the other hand, if the arithmetic mean molecular weight exceeds 40,000, a high solid content adhesive cannot be obtained.

[0020] Furthermore, if the arithmetic mean molecular weight of the aforementioned oligomer is less than 300, achieving a tack-free adhesive layer before thermal lamination will be difficult. On the other hand if the arithmetic mean molecular weight exceeds 5000, the property of hardening by electron beam will be reduced.

[0021] The formulation amount of oligomer in 100 weight parts of polyester resin is between 2 and 200 weight parts, preferably between 5 and 100 weight parts, and even more preferably between 10 and 50 weight parts. If the formulation amount is less than 2 weight parts, the electron beam-hardening reaction of the adhesive will be insufficient and properties such as retort resistance will be reduced. On the other hand, if the formulation amount exceeds 200 weight parts, achieving a tack-free adhesive layer prior to thermal lamination will be difficult. Furthermore, thermal stability during heat treating of the film-laminated metal plate after electron beam irradiation will deteriorate.

[0022] Examples of the aforementioned stress-relaxing agent which is added to the resin composition consisting of polyester resin and oligomer include silica ($SiO_2 \cdot nH_2O$), bentonite ($Al_2O_3 \cdot 5SiO \cdot 2H_2 O$), clay ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), talc ($3MgO \cdot 4SiO_2 \cdot 2H_2O$), barium sulfate ($BaSO_4$), and calcium carbonate ($CaCO_3$), and the like.

[0023] If an adhesive containing these stress-relaxing agents is used to manufacture a film-laminated metal plate, the retort resistance of the processing region of the metal plate will be improved. The reason that the retort resistance improves is thought by the present inventors to be because the stress-relaxing agent in the adhesive relieves the stress that occurs during process forming of the metal plate, thus maintaining the stability of the adhesive layer.

[0024] Of the aforementioned stress-relaxing agents, extremely fine silica with a particle size between 0.01 and 0.002 microns has higher stress-relaxing effect and is preferable. The formulation amount of stress-relaxing agent is between 0.5 and 250 PHR (weight parts in the 100 weight parts of resin) preferably between 20 and 100 PHR based on the resin composition consisting of polyester resin and oligomer. If the formulation amount of the stress-relaxing agent is less than 0.5 PHR, there will not be a noticeable increase in the retort resistance in the forming region of the film-laminated metal plate, but on the other hand, if the formulation amount exceeds 250 PHR, the adhesive properties of the adhesive will be reduced.

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[0025] Furthermore, the electron beam-hardening adhesive of the present invention may contain colored pigment (for instance white pigments such as titanium oxide, or a commonly known colored pigment which is used by mixing with said white pigment) if necessary and may be used as both a colored coating and an adhesive. With the present invention, the film-laminated metal plate has an ink layer, and if this ink layer is used as the outer surface of a can, normally a colored layer (normally a white coat) is required beneath a printed ink layer formed by multi-color printing, but if a colored coating adhesive is used, one step can be eliminated from the can manufacturing process, which is extremely advantageous. With the present invention, the electron beam-hardening adhesive is a blend of a resin composition consisting of polyester resin and oligomer with a stress-relaxing agent and if necessary a colored pigment, and is diluted as needed using an organic solvent such as methyl ethyl ketone, or toluene, or the like. Furthermore, the retort resistance of the film-laminated metal plate can be increased by formulating the resin component in the adhesive to have 30% by weight or less of a vinyl resin such as vinyl chloride resin, vinyl acetate resin, vinyl chloride/vinyl acetate copolymer, vinylidene chloride resin, or the like, or a (block) polyisocyanate compound.

[0026] With the present invention, the electron beam-hardening ink is comprising a colorant and a resin composition formulated to have between 2 and 200 weight parts of polyethylene oligomer with an arithmetic mean molecular weight between 300 and 5000 and having between 0.3 to 5.0 mol/kg molecules with polymeric unsaturated double bonds in 100 weight parts of polyester resin.

[0027] The same polyester resin as the polyester resin which is the electron beam-hardening adhesive component may be used as the aforementioned polyester resin. If the arithmetic mean molecular weight of the polyester resin is below 7000, the ink will tend to have poor water resistance, but on the other hand, if the arithmetic mean molecular weight exceeds 40,000, the viscosity will be high and handling will be difficult.

[0028] Furthermore, the same polyester oligomer as the polyester oligomer which is the electron beam-hardening adhesive component may be used as the aforementioned polyester oligomer. If the arithmetic mean molecular weight of the oligomer is less than 300, the ink layer will not easily achieve a tack-free condition and the ink will easily smear, but on the other hand, if the arithmetic mean molecular weight exceeds 5000, electron beam-hardening properties will be reduced.

[0029] If the formulation amount of the polyester oligomer in the electron beam-hardening ink is less than 2 weight parts in 100 weight parts of polyester resin, the hardening reaction by the electron beam will be insufficient and properties such as retort resistance will be reduced, but if the amount exceeds 200 weight parts, the ink layer will not easily achieve a tack-free condition, and the ink will easily smear.

[0030] The colorant used in the electron beam-hardening ink may be any colored pigment or dye normally used to color inks, and either organic or inorganic substances are acceptable. The amount of colorant is not particularly restricted, but normally is within a range between 5 and 300 weight parts in 100 weight parts of total solid content of polyester resin and polyester oligomer.

[0031] If necessary, a stress-relaxing agent which was suggested as a component of the aforementioned electron beam-hardening adhesive may be added to the electron beam-hardening ink. The formulation amount for this stress-relaxing agent is preferably 100 weight parts or less with regards to 100 weight parts of total content of polyester resin and polyester oligomer. Furthermore, the electron beam-hardening ink may be formulated with an organic solvent if necessary, such as methyl ethyl ketone or toluene, or the like.

[0032] Furthermore, in order to increase the retort resistance of the film-laminated metal plate, the resin composition of the electron beam-hardening ink may have 30% by weight or less of a vinyl resin such as vinyl chloride resin, vinyl acetate resin, vinyl chloride resin/vinyl acetate copolymer, vinylidene chloride resin, or the like, and (block) polyisocyanate compound.

[0033] With the present invention, a PET film may be suggested as a representative example of the transparent plastic film which is laminated onto the metal plate using electron beam-hardening adhesive. Between 75 and 100% of the ester repeating units of the PET film consist of ethylene terephthalate units, and ester units such as phthalic acid, isophthalic acid, succinic acid, and adipic acid, and the like, may be suggested as the ester units other than ethylene terephthalate. PET film surface is normally surfaced treated with a Corona discharge treatment, or the like, in order to increase adhesion to the adhesive. Furthermore, with the present invention, a polyethylene film or a polypropylene film, or the like, may be used as the transparent plastic film instead of a PET film.

[0034] With the present invention, examples of the metal plate include hot rolled plate, cold rolled plate, melted zinc or zinc alloy galvanized steel plate, electroplated zinc or zinc alloy galvanized steel plate, tin plate, tin-free steel, chrome-plated sheet steel, aluminum-plated sheet steel, tungsten-plated sheet steel, nickel-plated sheet steel, and other types of alloy-plated sheet steel, stainless steel, aluminum plate, copper plate, titanium plate, and other metal plates, and if necessary these plates may have a chemical treatment such as phosphoric acid treatment, chromate treatment, organic chromate treatment, cobalt complex oxide treatment, nickel substitution plating, and other treatments. Furthermore, metal plate which has a color coating such as a white coat on the surface of the aforementioned metal plates or chemically treated metal plates are included in the metal plate of the present invention. The color coating such as white coat becomes the base layer for printing, and the color coating such as white coat can be used as a base layer for printing on the outside surface of the can.

[0035] Next, an example of a manufacturing method for the film-laminated metal plate will be described. First, electron beam-hardening ink with the desired color is applied at a thickness of between 0.5 and 3 μm using for instance a gravure offset method onto a corona discharge treated PET film with a thickness between 5 and 30 μm, the film is dried to a tack-free condition by heating for several seconds at a temperature between 50°C and 150°C if necessary, a different colored electron beam-hardening ink is similarly applied and dried, in order to perform two color printing on the PET film. Furthermore, a colored coating and electron beam-hardening adhesive into which, for instance, titanium oxide is dispersed, or an electron beam hardened transparent adhesive without colored pigment is applied to a dried film thickness of between 1 and 5 μm using a normal painting means such as a roll coating method, gravure method, gravure offset method, or spray painting, or the like, and then dried, if necessary, for several seconds at a temperature of between 50°C and 150°C until a tack-free condition is achieved. Next, the adhesive layer is overlaid onto a metal plate (for instance, tin plate), and thermally laminated at a temperature below the thermal softening temperature for PET film (less than approximately 230°C) for approximately two seconds or less, in order to obtain a laminated steel plate.

[0036] An electron beam is irradiated through the PET film onto the laminated metal plate obtained thereby in order to harden the film and obtain the objective film-laminated metal plate, and the accelerator of the electron beam-generating source used to a radiate the electron beam may be a Cockcroft accelerator, Cockcroft-Walton accelerator, Van de Graaff accelerator, resonance transformer, transformer, insulated core transformer, Dynamitron, linear fillament, area beam accelerator or high frequency accelerator, or the like. The electron beam energy required to harden the electron beam-hardening adhesive and ink of the present invention is between 100 KeV and 300 KeV, and preferably a range between 150 KeV and 200 KeV is appropriate. A beam intensity of between 0.2 Mrad and 15 Mrad is appropriate, and between 1 Mrad and 5 Mrad is particularly preferable. The irradiation time for the electron beam is normally less than approximately 1 second, which is approximately 1/50th of the time required for thermal hardening.

[0037] The film-laminated metal plate obtained is suitable for use in various types of cans such as cans for beverages, cans for food, 5 gallon cans, and the like. Furthermore, applications such as thermos bottles and refrigerator outside surfaces are also possible.

[0038] PREFFERED EMBODIMENTS

The present invention will be described below using preferred embodiments.

[0039] Manufacturing Polyester Resin

Manufacturing Example 1

18.3 weight parts of dimethyl terephthalate, 11.7 weight parts of dimethyl isoterephthalate, 11.9 weight parts of ethylene glycol, 20.5 weight parts of neopentyl glycol, 118 mg of zinc acetate dihydrate as an ester substitution catalyst, and 246 mg of antimony trioxide as a condensation polymerization catalyst were added to a 1 L autoclave, heated to between 160°C and 210°C, subjected to ester substitution reaction, and the ester substitution reaction was completed two hours later when a stoichiometric amount of methanol had been distilled. Then, a small quantity of trimethyl phosphate was added and mixed for 30 minutes at between 200°C and 210°C. Next, the temperature was increased to 220°C, and 37.6 weight parts of azelaic acid were added and the ester reaction was continued for 30 minutes at a temperature between 220°C and 230°C. Next, the pressure was gradually reduced while the temperature was increased to 250°C, and the excess glycol was removed at 250°C 10 mm Hg. The temperature was further increased and the pressure decreased until obtaining polyester resin (I) with an OH value of 6.5 and an arithmetic mean molecular weight of 30,000. Furthermore, this resin (I) was diluted with a solvent consisting of methyl ketone/cyclohexanone = 50/50 until the heating residue was 30% by weight.

[0040] Manufacturing Example 2

A polyester resin (II) solution was synthesized in accordance with Manufacturing Example 1, using the following composition.

dimethyl terephthalate	22.2 weight parts
dimethyl isophthalate	32.7 weight parts
sebacic acid	19.0 weight parts
ethylene glycol	10.1 weight parts
neopentyl glycol	26.2 weight parts

The arithmetic mean molecular weight of the resin (II) obtained was 25,000.

[0041] Polyester Oligomer Manufacturing Example

Manufacturing Example 3

1.0 moles of trimethylol propane, 2.0 moles of triethylene glycol, 1.0 moles of 1,6-hexanediol, 3.0 mol of adipic acid, and catalytic quantities of dibutyl tin compound were combined, and a polyester with a arithmetic mean molecular weight of approximately 850 and a hydroxyl value of 200 was produced using a commonly known manufacturing method. Next, the polyester obtained was blended with acrylic acid to a ratio of 1.25 equivalents of acrylic acid to 1.0 equivalents of polyester hydroxyl groups, 100 ppm of a polymerization inhibitor (hydroquinone) was added and a reaction proceeded at between 80°C and 100°C, and after the reaction had stopped at a conversion ratio of approximately 85% by weight, the solvent and unreacted acrylic acid were removed by evaporation, and a polyester acrylate oligomer (I) with approximately 3.0 mol/kg molecule of polymeric double bonds was obtained.

[0042] Manufacture of Electron Beam-Hardening Ink (Manufacturing Examples 4 through 7)

Manufacturing Example 4

30 weight parts of red pigment (product name "Red 500 RG," product of Tosoh Corporation) and 20 weight parts of silica (product name "Aerosil 300," product of Japan Aerosil) were added to a resin composition consisting of 10 weight parts of polyester acrylate oligomer (I) in 330 weight parts of a 30% by weight polyester resin (I) solution, and the solid content was adjusted to make a 35% by weight solution using methylethyl ketone solvent to make ink R-1.

[0043] Manufacturing Example 5

30 weight parts of blue pigment (product name "Cyanine Blue 5240," product of Dainichiseika Color and Chemicals Mfg. Ltd.) and 20 weight parts of silica (same as Manufacturing Example 4) were added to a resin composition consisting of 30 weight parts of polyester acrylate oligomer (I) in 330 weight parts of a 30% by weight polyester resin (II) solution, and the solid content was adjusted to make a 35% by weight solution using methyl ethyl ketone solvent to make ink B-1.

[0044] Manufacturing Example 6

Ink R-2, a solution with a solid content of 35% by weight, was obtained by the same method as Manufacturing Example 4, except that the formulation amount of polyester acrylate oligomer (I) in Manufacturing Example 4 was changed from 10 weight parts to 20 weight parts, and silica was not added.

[0045] Manufacturing Example 7

Ink B-2, a solution with a solid content of 35%, was obtained by the same method as Manufacturing Example 5, except that the formulation amount of polyester acrylate oligomer (I) in Manufacturing Example 5 was changed from 30 weight parts to 20 weight parts.

[0046] Manufacture of Electron Beam-hardening Adhesive (Manufacturing Examples 8 through 12)

Manufacturing Example 8

80 weight parts of silica (product name "Aerosil 300," product of Japan Aerosil) was added to a resin composition consisting of 20 weight parts of polyester acrylate oligomer (I) in 330 weight parts of a 30% by weight polyester resin (I) solution, and the solid content was adjusted to make a 30% by weight solution using methylethyl ketone solvent. (Adhesive A)

[0047] Manufacturing Example 9

40 weight parts of the silica used in Embodiment 1 was added to a resin composition consisting of 60 weight parts of polyester acrylate oligomer (I) in 330 weight parts of a 30% by weight polyester resin (II) solution, and the solid content was adjusted to make a 30% by weight solution using methylethyl ketone solvent. (Adhesive B)

[0048] Manufacturing Example 10

100 weight parts of barium sulfate (product name "Bari-fine," product of Sakai Chemical Industry Co. Ltd.), 10 weight parts of vinyl chloride resin (product name "VERR," product of Union Carbide), and 10 weight parts of polyester acrylate oligomer (I) were added to 330 weight parts of a 30% by weight polyester resin (I) solution, and the solid content was adjusted to make a 30% by weight solution using methylethyl ketone solvent. (Adhesive C)

[0049] Manufacturing Example 11

Using the Adhesive A prepared in Manufacturing Example 8, titanium white pigment JR-300 (product of Teikoku Chemical) was dispersed to form a pigment/binder weight ratio = 2 to produce a white coat adhesive. The solid content of the paint was adjusted to 45% by weight. (Adhesive D)

[0050] Manufacturing Example 12

Adhesive E with a solid content of 30% was obtained similar to Manufacturing Example 8, except that the silica of Manufacturing Example 8 was not added.

[0051] Manufacture of Film-laminated Metal Plate

Embodiment 1

The ink R-1 obtained in Manufacturing Example 4 was applied by the gravure offset method to a thickness of approximately 1 μm to make a pattern on the corona discharge treated surface of Ester Film E5100 (12 μm thick PET film) produced by Toyobo Co. Ltd. (corona discharge treated on one side), passed through a drying oven for five seconds at 100°C, and then the ink B-1 obtained in Manufacturing Example 5 was similarly applied and dried. Next, Adhesive A was applied to a thickness of between 2 and 4 μm using gravure application across the entire surface of the PET film with ink layer. The film was then passed through a drying oven for 10 seconds at 100°C to evaporate the solvent component leaving a tack-free condition. This painted PET film and a 0.19 mm thick tin plate Canlite (product of Nippon Steel Corp.) were thermal laminated at a roller pressure force of 5.0 kilograms/cm^2 and a roller temperature of 180°C. Finally, an electron beam was irradiated through the PET film of the laminated metal plate at a current of 50 mA, an intensity of 4 Mrad, and an acceleration voltage of 270 KeV using an electron beam accelerator to harden the adhesive layer and the ink layer in order to obtain a film-laminated metal plate.

[0052] Embodiments 2 ~ 10 and Comparative Examples 1 ~ 3

A film-laminated metal plate was obtained by the same method as Embodiment 1 using the conditions shown in Table 1.

[0053] Welded cans were produced using the film-laminated metal plates obtained by the embodiments and comparative examples with the polyester film as the outer surface of the can body, and then necking was performed to the first stage, second stage, third stage, and fourth stage, and finally bead processing was performed to crimp the lid closed.

[0054] The film-laminated metal plate and can obtained as shown above were subjected to various performance tests, and the results are shown in Table 1. Note, the test methods were as shown below.

[0055] (1) Adhesion 180°C peel: In accordance with JIS K-6744. The peel strength is shown.

[0056] (2) Processability (Dupont impact test): The PET film surface was struck from behind using a 1/2 inch 500 g weight from a height of 50 cm, and the test sample was observed to confirm no peeling between the metal plate and the PET film. Favorable tests where no peeling was observed were evaluated as O.

[0057] (3) Retort resistance: a film-laminated metal plate that had been Erichsen deep draw processed for a beverage can was exposed in tap water steam at an autoclave pressure of 1.4 atm, 125°C x 30 minutes, and then the whitening and adhesive properties were evaluated. The deep drawn conditions were: cutout diameter D60 mm, diameter d33 mm, clearance 0.2 mm, and press force 500 kg/cm^2. Furthermore, a 200 mm diameter welded can formed using the film-laminated metal plate was filled with water and sealed at an autoclave pressure of 1.4 atm, 120°C x 30 minutes and exposed to tap water steam, and the condition of the seam line in the welded area of the can surface and the general surface appearance were visually observed. Favorable tests with no problems were evaluated as O.

[0058] (4) Thermally stable film-laminated metal plate was cut into 5 cm x 5 cm dimensions, heat treated at 200°C for two minutes, and the degree of thermal contraction of the PET film was observed. Tests with no problems or with low thermal shrinkage were evaluated as O.

[0059] Table 1

	Ink type		Adhesive		Electron Beam Irradiation Conditions			Adhesion	Processability	Retort resistance				Thermal stability
	Red	Blue	Type	Thickness (μm)	Voltage KeV	Current mA	Intensity Mrad	180° peel test (g/15 mm)	DuPont impact	Whitening	Adhesion	Seam line condition	Appearance	
Embodiment 1	R-1	B-1	A	3	270	50	4	500	O	O	O	O	O	O
Embodiment 2	R-2	B-2	A	3	250	40	5	550	O	O	O	O	O	O
Embodiment 3	R-1	B-2	A	2	250	40	3	600	O	O	O	O	O	O
Embodiment 4	R-2	B-1	A	4	270	50	4	500	O	O	O	O	O	O
Embodiment 5	R-2	B-1	B	3	270	50	4	450	O	O	O	O	O	O
Embodiment 6	R-1	B-2	B	2	250	40	3	500	O	O	O	O	O	O
Embodiment 7	R-1	B-1	C	3	270	50	4	500	O	O	O	O	O	O
Embodiment 8	R-2	B-2	C	4	270	50	5	600	O	O	O	O	O	O
Embodiment 9	R-2	B-1	D	3	270	50	4	500	O	O	O	O	O	O
Embodiment 10	R-1	B-2	D	2	250	40	3	450	O	O	O	O	O	O
Comparative Example 1	R-162*1	R-39*2	A	3	270	50	4	400	O	Slight whitening of the processing area	30% pealing in the processing area	O	O	O
Comparative Example 2	R-162*1	R-39*2	B	3	270	50	4	400	O	Slight whitening of the processing area	30% pealing in the processing area	O	O	O
Comparative Example 3	R-1	B-1	E	3	270	50	4	350	O	O	30% pealing in the processing area	O	O	O

[0060] The (Notes) in Table 1 are as shown below.

*1 R162: standard laminating ink, product name "Lamistar R162 Red," color red, produced by Toyo Ink Manufacturing.

*2 R39: standard laminating ink, product name "Lamistar R39 Indigo," color blue, produced by Toyo Ink Manufacturing.

[0061] EFFECT OF THE INVENTION

The film-laminated metal plate obtained by the present invention has excellent adhesion between the plastic film, ink, and metal plate, and has excellent retort resistance and particularly retort resistance in the forming region when used as a can for foods. Furthermore, if a plastic film with an ink layer is laminated onto a metal plate using the polyester resin electron beam-hardening adhesive of the present invention, there are advantages in that the process can be performed at high speed and low temperature, and because electron beam hardening is possible, the hardening time for the ink and the adhesive can be dramatically shortened, and as a result plant space can be greatly conserved. Moreover, with the present invention, hardening of the ink and the adhesive does not require that the electron beam irradiation environment be a perfect nitrogen environment, so there is the advantage that the electron beam hardening can be performed in air.

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(54) TITLE OF THE INVENTION

Electron Beam-Hardening Adhesive and Polyester Film Laminated Metal Plate Making Use Thereof

(57) ABSTRACT

PURPOSE

To obtain an adhesive layer which can be used for a long period of time to manufacture a PET laminate metal plate with excellent blocking resistance, and favorable adhesion, processability, and retort resistance.

RESOLUTION MEANS

An electron beam-hardening adhesive containing:

(a) 100 weight parts of a polyester resin obtained by the addition reaction of a polybasic acid with a polyester polymer containing hydroxyl groups, having an arithmetic mean molecular weight of between 10,000 and 40,000, a weighted mean molecular weight to arithmetic mean molecular weight ratio (Mw/Mn) of between 2.5 and 7.0, a glass transition temperature of between 20°C and 55°C, a hydroxyl value of between 3 and 15 KOH mg/g, and an acid value of between 5 and 30 KOH mg/g: and

(b) between 3 and 30 weight parts of polymeric unsaturated oligomer having between 5 and 15 mol/kg of polymeric unsaturated double bonds, an arithmetic mean molecular weight of between 200 and 2000, and a hydroxyl value of between 0 and 200 KOH mg/g;

and also a polyester film laminated metal plate wherein a polyester film which may have an ink layer is laminated using said adhesive.

EXTENT OF PATENT CLAIMS

What Is Claimed Is:

Claim 1

An electron beam-hardening adhesive containing:

(a) 100 weight parts of a polyester resin obtained by the addition reaction of a polybasic acid with a polyester polymer containing hydroxyl groups, having an arithmetic mean molecular weight of between 10,000 and 40,000, a weighted mean molecular weight (Mw) to arithmetic mean molecular weight (Mn) ratio (Mw/Mn) of between 2.5 and 7.0, a glass transition temperature of between 20°C and 55°C, a hydroxyl value of between 3 and 15 KOH mg/g, and an acid value of between 5 and 30 KOH mg/g: and

(b) between 3 and 30 weight parts of polymeric unsaturated oligomer having between 5 and 15 mol/kg of polymeric unsaturated double bonds, an arithmetic mean molecular weight of between 200 and 2000, and a hydroxyl value of between 0 and 200 KOH mg/g.

Claim 2

The electron beam-hardening adhesive according to Claim 1, further containing between 2 and 10 weight parts of unblocked polyisocyanate compound and between 0 and 20 weight parts of blocked polyisocyanate compound in a total of 100 weight parts of polyester resin (a) and polymeric unsaturated oligomer (b).

Claim 3

The electron beam-hardening adhesive according to Claim 1 or Claim 2, further containing between 1 and 50 weight parts of an antiblocking agent in a total of 100 weight parts of polyester resin (a) and polymeric unsaturated oligomer (b).

Claim 4

The electron beam-hardening adhesive according to any one of Claims 1 through 3 further containing between 50 and 250 weight parts of white pigment in a total of 100 weight parts of polyester resin (a) and polymeric unsaturated oligomer (b).

Claim 5

A polyester film laminated metal plate made by laminating a polyester film which may have an ink layer onto one or both sides of a metal plate using said electron beam-hardening adhesive shown in Claim 1.

Claim 6

A manufacturing method for a polyester film laminated metal plate comprising:

(1) a step of applying and drying said adhesive shown in Claim 1 onto a polyester film (A) which may have an ink layer;

(2) a step of rolling the polyester film having a dried adhesive layer into a coil; and

(3) a step of uncoiling the polyester film having an adhesive layer which was rolled in a coil, aligning the adhesive layer surface of the polyester film to contact one surface or both surfaces of the metal plate and performing thermocompression bonding.

Claim 7

The manufacturing method for a polyester film laminated metal plate according to Claim 6, further comprising (4) a step of hardening the adhesive layer by irradiating an electron beam onto the thermocompressed adhesive layer.

DETAILED DESCRIPTION OF THE INVENTION

[0001] TECHNICAL FIELD OF THE INVENTION

The present invention relates to an electron beam-hardening adhesive which can form an adhesive layer for a polyester film laminate metal plate with excellent appearance, adhesion to the metal plate, blocking resistance, and can be used for long period of time, as well as to a polyester film laminate metal plate which uses said electron beam-hardening adhesive and to a manufacturing method for said laminate metal plate.

[0002] BACKGROUND TECHNOLOGY AND PROBLEM TO BE RESOLVED BY THE INVENTION

Conventionally, metal plate which has been laminated with a polyester film which is used for cans for beverages and cans for food (hereinafter referred to as "PET laminate metal plate") normally consists of a metal plate overlaid with a polyester film using an adhesive (for instance, refer to Japanese Unexamined Patent Application H3-87249, and the like).

[0003] A conventional PET laminate metal plate, for instance, is made by (1) a step of printing ink, if necessary, on a polyester film which is a transparent plastic film, drying, applying an adhesive thereon, and then drying until tack-free (normally at approximately 50°C to 150°C for several seconds); or (2) a step of hardening by heating (normally at approximately 160°C to 170°C for approximately 0.5 seconds) and compressing a polyester film onto which an adhesive layer has been formed, onto a metal plate.

[0004] However, the aforementioned conventional manufacturing method has the following problems.

[0005] 1. In order to meet conditions for manufacturing PET laminate metal plate using a high-speed production line necessary for large volume production, the baking oven must be lengthened and this equipment is large so the equipment expense will increase and more plant space will be required.

[0006] 2. With a conventional manufacturing method, if the lamination speed exceeds 150 m/min, or if the lamination temperature is below 160°C, areas without sufficient adhesion will appear, and variations in appearance will easily occur.

[0007] 3. A can for beverages or a can for food manufactured from PET laminated metal plate obtained by a conventional method has poor processing properties (necking process, flanging process, beading process, and the like) and because of the heat from baking (maximum temperature between 230°C and 280°C for between approximately 7 and 100 seconds) the side seam paint (paint for repairing the weld region) and the heat of welding at the can body seam line in the area of the weld, whitening or blistering may occur after retort processing, a pattern similar to water spots may appear on the surface of the polyester film, and surface finish will readily be degraded because of reduced gloss, and the like.

[0008] In order to resolve the aforementioned problems, the present inventors have previously proposed in Japanese Unexamined Patent Application H6-192637 a method for obtaining a film laminated metal plate using an electron beam hardened adhesive as the adhesive, and after laminating a polyester film having an ink layer onto a metal plate using the electron beam-hardening adhesive, an electron beam is irradiated through the polyester film in order to harden the adhesive.

[0009] The aforementioned problems can be resolved by the method according to this proposal. However, the aforementioned polyester film laminated with an ink layer and an adhesive layer (hereinafter also abbreviated as "lamination film") is normally rolled in a coil after the adhesive is dry, stored until the time of use, and then uncoiled and applied to a metal plate at the time of use, but the lamination film according to the aforementioned proposal experiences large changes in the degree of hardness of the adhesive layer during storage and the adhesive forces between the adhesion layer and the metal plate may be weakened depending on the hardness, so there is a problem that the time period when the lamination film can be laminated to the metal plate is short. Furthermore, if an attempt is made to minimize the change in the degree of the hardness of the adhesive layer to lengthen the period that lamination is possible, of the short period after the lamination film is produced, if the film is laminated to the metal plate within, for instance, five days, appearance defects will easily occur due to wrinkling of the film, and problems with adhesive protruding out from the film surface will easily occur, so there is a problem that favorable lamination cannot be performed until after at least five days have passed as a curing period after the lamination film is produced, and thus the period that the lamination film can be used is severely restricted.

[0010] The present inventors have performed diligent research to obtain an adhesive which can resolve the aforementioned problems, can form a favorable laminate after approximately 1 day after the film is manufactured, and can form a laminate even after more than three months has passed after the laminate film was manufactured, such that a PET laminate metal plate made by laminating this laminate film onto a metal plate will have excellent performance for a PET laminate metal plate such as appearance, processability, adhesion between the polyester film and metal plate, and retort resistance.

[0011] As a result, the present inventors have discovered that the aforementioned objectives can be achieved by an electron beam-hardening adhesive consisting of specific polyester resins modified with polybasic groups and polymeric unsaturated oligomer, and have thus achieved the present invention.

[0012] MEANS FOR RESOLVING PROBLEMS

In other words, the present invention provides an electron beam-hardening adhesive containing:

(a) 100 weight parts of a polyester resin obtained by the addition reaction of a polybasic acid with a polyester polymer containing hydroxyl groups, having an arithmetic mean molecular weight of between 10,000 and 40,000, a weighted mean molecular weight (Mw) to arithmetic mean molecular weight (Mn) ratio (Mw/Mn) of between 2.5 and 7.0, a glass transition temperature of between 20°C and 55°C, a hydroxyl value of between 3 and 15 KOH mg/g, and an acid value of between 5 and 30 KOH mg/g: and

(b) between 3 and 30 weight parts of polymeric unsaturated oligomer having between 5 and 15 mol/kg of polymeric unsaturated double bonds, an arithmetic mean molecular weight of between 200 and 2000, and a hydroxyl value of between 0 and 200 KOH mg/g.

[0013] Furthermore, the present invention provides a polyester film laminated metal plate made by laminating a polyester film which may have an ink layer onto one or both sides of a metal plate using said electron beam-hardening adhesive.

[0014] Moreover, the present invention provides a manufacturing method for a polyester film laminated metal plate comprising:

(1) a step of applying and drying said electron beam-hardening adhesive on to a polyester film which may have an ink layer;

(2) a step of rolling the polyester film having a dried adhesive layer into a coil; and

(3) a step of uncoiling the polyester film having an adhesive layer which was rolled in a coil, aligning the adhesive layer surface of the polyester film to contact one surface or both surfaces of the metal plate and performing thermocompression bonding.

[0015]

PREFERRED EMBODIMENTS

The electron beam-hardening adhesive of the present invention will be described below in greater detail.

[0016] The adhesive of the present invention contains as essential components polyester resin (a) and polymeric unsaturated oligomer (b).

[0017] Polyester resin (a)

The polyester resin (a) is a polyester resin obtained by an ester reaction between a polybasic acid and a polyester prepolymer containing hydroxyl groups which is an esterified compound with a polybasic acid component and a polyhydric alcohol component as the main raw material components.

[0018] The polyester resin (a) suitably has an arithmetic mean molecular weight of between 10,000 and 40,000, preferably between 12,000 and 22,000, a weighted mean molecular weight (Mw) to arithmetic mean molecular weight (Mn) ratio (Mw/Mn) of between 2.5 and 7.0, preferably between 3.0 and 6.2, a glass transition temperature between 20°C and 55°C, preferably between 20°C and 40°C, a hydroxyl value of between 3 and 25 KOH mg/g, preferably between 5 and 15 KOH mg/g, and an acid value between 5 and 30 KOH mg/g, preferably between 8 and 20 KOH mg/g.

[0019] For the polyester prepolymer with hydroxyl groups used to manufacture the polyester resin (a) the polybasic acid component which is a main raw material component of the prepolymer is one or more types of dibasic acids selected from phthalic anhydride, iso-phthalic acid, terephthalic acid, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, succinic acid, fumaric acid, adipic acid, azelaic acid, subacid acid, decanedioic acid, maleic anhydride, itaconic acid, and dimer acid, and the like, as well as lower-level alkyl esters of these acids, and, if necessary, may be used in combination with polybasic acids with a hydroxyl value of 3 or higher, such as trimellitic anhydride, methylcyclohexene tricarboxylic acid, pyromellitic anhydride, and the like.

These polybasic acid components may be used individually, or two or more types may be blended and used. Furthermore, if necessary, a monobasic acid such as benzoic acid, crotonic acid, p-t-butyl benzoic acid, or the like, may be used in addition to the aforementioned polybasic acid components.

[0020] The polyhydric alcohol component which is a main raw material component of the polyester prepolymer with hydroxyl groups is primarily consisting of dihydric alcohols such as ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol, neopentyl glycol, 3-methylpentanediol, 1,4-hexanediol, 1,6-hexanediol, cyclohexanedimethanol, hydrogenated bisphenol A, ethylene oxide adducts of bisphenol A, and propylene oxide adducts of bisphenol A, and if necessary, polyhydric alcohols with a value of 3 or higher such as trimethylolethane, trimethylolpropane, and pentaerythritol, or the like, may also be used in combination. These polyhydric alcohols may be used individually, or two or more types may be blended and used.

[0021] The esterification reaction or ester substitution reaction between the aforementioned acid components and the polyvalent alcohol components may be performed using a previously known method; and, for instance, can be performed by polymeric condensation of the acid component and polyhydric alcohol component at a temperature of between approximately 180°C and 250°C.

[0022] The polyester prepolymer with hydroxyl groups obtained as described above has an arithmetic mean molecular weight between 9000 and 39,000, preferably between 11,000 and 21,000, and should have a hydroxyl value in a range between 8 and 45 KOH mg/g.

[0023] The polyester resin (a) can be manufactured by causing an addition reaction to occur between the polyester prepolymer with hydroxyl groups obtained as described above with a polybasic acid such as maleic acid, maleic anhydride, phthalic anhydride, trimellitic anhydride, adipic acid, azelaic acid, and dimer acid, or the like, partially esterifying a portion of the hydroxyl groups in the prepolymer, and introducing carboxyl groups. The polybasic acid used in the aforementioned partial esterification reaction is preferably an acidic anhydride. The partial esterification reaction may be performed by a previously known method, and, for instance, can be achieved by reacting the aforementioned polyester prepolymer with hydroxyl groups and a polybasic acid anhydride at a temperature between approximately 170°C and 190°C.

[0024] With the adhesive of the present invention, the polyester resin (a) may be one type of resin, or two or more may be blended and used together.

[0025] Polymeric Unsaturated Oligomer (b)

The polymeric unsaturated oligomer (b) has at least one, preferably between 2 and 4 polymeric unsaturated double bonds in each molecule, and the polymeric unsaturated double bonds are present in a concentration of between 5 and 15 mol/kg, preferably between 5 and 10 mol/kg, have an arithmetic mean molecular weight between 200 and 2000, preferably between 300 and 1500, and a hydroxyl value between 0 and 200 KOH mg/g, preferably between 30 and 80 KOH mg/g.

[0026] The type resin of the polymeric unsaturated oligomer (b) is not particularly restricted, and for instance, modified polyester resin, acrylic resin, modified urethane resin, modified epoxy resin, and the like, may be suggested.

[0027] The aforementioned modified polyester resin oligomer may be obtained, for instance, by ester bonding a polymeric unsaturated carboxylic acid such as acrylic acid with a low molecular weight polyester that has hydroxyl groups and that has an arithmetic mean molecular weight of approximately 1900 or less, in order to introduce polymeric double bonds. The aforementioned low molecular weight polyester containing hydroxyl groups can be obtained by polymeric condensation to a molecular weight within the aforementioned range using as the main raw materials the polyhydric alcohol component and polybasic acid component that were used when manufacturing the polyester prepolymer containing hydroxyl groups used to manufacture the aforementioned polyester resin (a). Commercial examples of modified polyester resin oligomer include Aronix M-7100, Aronix M-8100, and Aronix M-9050 (product names, product of Toagosei Co., Ltd.).

[0028] The aforementioned acrylic resin oligomer may be obtained, for instance, by reacting a low molecular weight acrylic resin that has functional groups such as hydroxyl groups, carboxyl groups, or epoxy groups, or the like, and that has an arithmetic mean molecular weight of approximately 1900 or less, with a polymeric unsaturated compound containing reactive groups that have polymeric unsaturated groups and reactive groups that are reactive towards the functional groups in the acrylic resin, under conditions such that the polymeric unsaturated groups are not eliminated, in order to introduce polymeric double bonds to a low molecular weight acrylic resin. Commercial examples of the aforementioned acrylic resin oligomer include Aronix M-305, and Aronix M-450 (product names, product of Toagosei Co., Ltd.).

[0029] The modified urethane resin oligomer can be obtained, for instance, by first reacting ethylene oxide with isocyanuric acid to introduce hydroxyl groups, and then reacting this isocyanurate acid which contains hydroxyl groups with a polymeric unsaturated compound which contains functional groups that are reactive towards the hydroxyl groups such as polymeric unsaturated compounds containing carboxyl groups such as acrylic acid in order to introduce polymeric unsaturated groups. Commercial examples of the aforementioned modified urethane resin oligomer include Aronix M-315, and Aronix M-215 (product names, product of Toagosei Co., Ltd.).

[0030] The modified epoxy resin oligomer can be obtained, for instance, by reacting a polymeric unsaturated compound containing carboxyl groups such as acrylic acid, or the like, with a compound containing at least one, preferably two or more epoxy groups, in order to introduce polymeric unsaturated groups.

[0031] With the adhesive of the present invention, the polymeric unsaturated oligomer (b) may be one type of resin, or two or more may be blended and used together.

[0032] With the adhesive of the present invention, the formulation amount of polymeric unsaturated oligomer (b) is suitably in a range between 3 and 30 weight parts, preferably in a range between 5 and 15 weight parts in 100 weight parts of the aforementioned polyester resin (a) from the viewpoint of hardness, adhesion, and blocking resistance.

[0033] The adhesive of the present invention contains as essential components the aforementioned polyester resin (a) and the polymeric unsaturated oligomer (b), and may consist of polyester resin (a) and polymeric unsaturated oligomer (b), but for the purpose of improving the application productivity of the adhesive, normally an organic solvent is added, and if necessary, for instance, hardening agents, hardening catalysts, anti-blocking agents, colored pigments, lubrication enhancers, silane coupling agents, defoaming agents, and antistatic agents, and the like, may be appropriately added.

[0034] The aforementioned organic solvents are substances which can dissolve or disperse the adhesive composition, and examples include hydrocarbon-based solvents such as toluene, xylene, and Solvesso #150 (product of Esso Petroleum, high boiling point hydrocarbon-based petroleum solvent), ketone-based solvents such as methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone, and ester-based solvents such as ethyl acetate, butyl acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate, ethylene glycol monoethyl ether acetate, and the like, and one or more of the solvents may be suitably selected and used.

[0035] The aforementioned hardening agent is a substance which can cause the adhesive to harden when heated by reacting with the polyester resin (a) or in some cases with the polymeric unsaturated oligomer (b), and for example, polyisocyanate compound and amino resins, or the like, may be suggested, but of these, polyisocyanate compounds are suitable from the viewpoint of adhesion with the PET film surface.

[0036] The aforementioned polyisocyanate compound may be an unblocked polyisocyanate compound where the isocyanate groups are unblocked, or may be a block polyisocyanate compound where at least one of the isocyanate groups in the molecule are blocked, and a mixture of these is also acceptable.

[0037] Specific examples of the aforementioned unblocked polyisocyanate compounds include aliphatic diisocyanates such as hexamethylene diisocyanate and trimethyl hexamethylene diisocyanate; cyclical aliphatic diisocyanates such as hydrogenated xylylene diisocyanate, isophorone diisocyanate; aromatic diisocyanates such as tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate; and polyisocyanate compounds which have three or more isocyanate groups such as triphenylmethane-4,4',4"-triisocyanate, 1,3,5-triisocyanate benzene, 2,4,6-triisocyanate toluene, 4,4'-dimethyl diphenylmethane-2,2',5,5'-tetraisocyanate, and other organic polyisocyanates, in an unmodified condition or as an adduct between these organic polyisocyanate and a polyhydric alcohol, low molecular weight polyester resin, or water, or the like, as well as cyclical compounds of the aforementioned organic polyisocyanate compounds with other organic polyisocyanate compounds, and also isocyanate biurets. Of these, an isocyanate that is a cyclopolymer of hexamethylene diisocyanate is preferable for use.

[0038] The blocked isocyanate compound is an isocyanate wherein at least one of the isocyanate groups of the aforementioned polyisocyanate compound molecules is blocked by a blocking agent, and has at least one blocked isocyanate group in the molecule, but may or may not have blocked isocyanate groups. **[Translator's Note: Possible mistake in the Japanese. Probably should read "but may or may not have unblocked isocyanate groups."]**

[0039] Examples of the aforementioned blocking agents include phenols such as phenol, cresol, and xylenol; lactams such as epsilon caprolactam, delta-valerolactam, gamma-butyrolactam, and beta-propiolactum; alcohols such as methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, tert-butyl alcohol, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monoethyl ether, propylene glycol monomethyl ether and benzyl alcohol; oximes such as formamidoximes, acetoaldoxime, acetoxime, methylethyl ketoxime, diacetylmonoxime, benzophenone oxime and cyclohexane oxime; active methylenes such as dimethyl malonate, diethyl malonate, ethyl acetoacetate, methyl acetoacetate, and acetylacetone, and the like. Of these, oxime blocking agents are most suitably used.

[0040] If a hardening agent is added, the formulation amount is preferably within a range below 30 weight parts in a total of 100 weight parts of the aforementioned components (a) and (b).

[0041] If a polyisocyanate compound is used as the hardening agent, a range of between 2 and 10 weight parts of unblocked polyisocyanate compound and a range between 0 and 20 weight parts of blocked polyisocyanate compound in a total 100 weight parts of the aforementioned component (a) and component (b) is suitable. By using both unblocked polyisocyanate compound and block polyisocyanate compound as the hardening agent, normally a balance can easily be achieved between hardness, lamination at high speed, and length of time that the PET film can be used.

[0042] The aforementioned hardening catalyst added in order to promote the reaction of the hardening agent, and if the hardening agent contains blocked polyisocyanate compound, organic metal catalysts such as tin octylate, dibutyltin di(2-ethylhexanoate), dioctyltin di(2-ethylhexanoate), dibutyltin dilaurate, dibutyltin oxide, dioctyltin oxide, and lead 2-ethylhexanoate, or the like, may be suitably used. If a hardening catalyst is added, the formulation amount is preferably within a range between 0.01 and 5 weight parts in a total of 100 weight parts of the aforementioned component (a), component (b), and a hardening agent.

[0043] The aforementioned antiblocking agent may be added, if necessary, in order to prevent adhesion and blocking from occurring between the adhesive layer and the adhesive-free surface of the PET film where an adhesive was not applied, which causes uncoiling to be difficult when an adhesive is applied to a PET film and the dried laminate film for laminating the metal plate is rolled in a coil and then uncoiled, or to prevent the adhesive from adhering to the PET film surface when being uncoiled.

[0044] Examples of the aforementioned antiblocking agent include body pigments such as fine silica powder, barium sulfate, calcium carbonate, talc, mica, and clay; polyolefin fine particles such as polyethylene fine particles, acid modified polyethylene fine particles, maleinized polypropylene fine particles, and polypropylene fine particles; and organic resin fine particles such as nylon fine particles, acrylic resin fine particles, silicone rubber fine particles, urethane resin fine particles, phenol resin fine particles, and polytetrafluoroethylene fine particles, and the like. The aforementioned organic resin fine particles have an average particle diameter of between 0.1 and 40 μm, preferably between 1 and 10 μm, and the softening point is preferably in a range between 100 and 200°C, and the resin type is most preferably polyethylene, polypropylene, or nylon.

[0045] If the aforementioned antiblocking agents are added, the formulation amount is normally within a range between 0.1 and 50 weight parts in a total of 100 weight parts of the aforementioned polyester resin (a) and polymeric unsaturated oligomer (b), and if the antiblocking agent is a body pigment, a range between 10 and 50 weight parts is preferable, in a range between 10 and 40 weight parts is more preferable, but if the antiblocking agent is organic resin particles, a suitable amount is between 0.1 and 30 weight parts, more preferably within a range between 1 and 20 weight parts. If the amount of antiblocking agent added is too high, the thermal softening of the adhesive layer will be reduced and the adhesive force between the PET film adhesive and the metal plate will be reduced, and lamination may not be possible, and furthermore, when the PET laminated metal plate or formed part thereof is subjected to retort processing, the PET film will easily peel from the metal plate.

[0046] The aforementioned colored pigment may be a white pigment such as titanium oxide, or a different colored pigment, or a glitter pigment such as aluminum powder. If the PET laminate metal plate is used as the outside surface of a can, normally multicolor printing is performed and a colored layer (normally a white coat) is required under the printing ink layer, but if an adhesive with a colored pigment and particularly a white pigment is used, the adhesive may also act as a white coat, and therefore one step of the can manufacturing process can be eliminated, which is extremely advantageous. The amount of colored pigment added is not particularly restricted so long as the level is within a range which does not hinder the performance of the adhesive layer, and normally, a quantitative range below 250 weight parts in a total of 100 weight parts of polyester resin (a) and polymeric unsaturated oligomer (b) is appropriate, and for white pigments, normally a range between 50 and 250 weight parts is preferable.

[0047] The aforementioned lubrication-enhancing agent is added to provide lubrication to the surface of the adhesive, and is added in order to allow smooth coiling of the adhesive coated lamination film for laminating metal plate, and to prevent sticking of the adhesive layer surface when the coil is unrolled. Examples of the lubrication-enhancing agent include aliphatic ester waxes; polyolefin waxes such as polyethylene wax; animal waxes such as lanolin or beeswax; plant waxes such as carnauba wax and water wax, and other waxes such as microcrystalline wax, silicon wax, and fluorine wax, and the like.

If a lubrication-enhancing agent is added, the formulation amount is preferably within a range between 0.01 and 10 weight parts in a total of 100 weight parts of the aforementioned components (a) and (b).

[0048] The aforementioned electron beam-hardening adhesive of the present invention is particularly suitable as an adhesive for use in polyester film laminated metal plates.

[0049] The polyester film laminated metal plate of the present invention has a polyester film which may have an ink layer laminated onto one or both sides of a metal plate using the adhesive layer. The adhesive layer must be electron beam hardened by the final product stage, but at the stage of the polyester film laminated metal plate, the adhesive layer may be, but is not required to be, electron beam hardened.

[0050] Next, the manufacturing method for the polyester film laminate metal plate will be described in detail.

[0051] The manufacturing method for the polyester film laminate metal plate of the present invention is comprising:
(1) a step of applying and drying the electron beam-hardening adhesive of the present invention onto a polyester film which may have an ink layer;
(2) a step of rolling the polyester film (A) having a dried adhesive layer into a coil; and
(3) a step of uncoiling the polyester film having an adhesive layer which was rolled in a coil, aligning the adhesive layer surface of the polyester film to contact one surface or both surfaces of the metal plate and performing thermocompression bonding.

[0052] The polyester film (A) which may have an ink layer in the aforementioned step (1) (hereinafter also referred to as "polyester film (A)") may be a simple polyester film without an ink layer, or may have an ink layer formed on the polyester film.

[0053] The aforementioned polyester film preferably has between 75 and 100% of ester repeating units made of ethylene terephthalate units, and ester units. Phthalic acid, isophthalic acid, succinic acid, and adipic acid, and the like, may be suggested as the ester unit acid component that is not ethylene terephthalate. The polyester film may be surfaced treated such as with a corona discharge treatment on the surface in order to improve adhesion with the ink or the adhesive, but not performing a surface treatment is preferable. The film thickness of the polyester film is not particularly restricted, but normally a film thickness of between approximately 5 and 30 μm is preferably used.

[0054] If an ink layer is formed on the polyester film, the ink which forms the ink layer may be an ink used for polyester films, and may be either a thermal hardening or activation beam-hardening ink. The ink may be applied as one color, or by overlaying two or more colors of ink.

[0055] The ink layer may be formed by printing the ink using a gravure printing method, for instance, and if necessary, removing the solvents and hardening by heating or by irradiating with an activation light beam.

[0056] A lamination film for laminating metal plate can be obtained by applying the adhesive of the present invention on to a polyester film (A) (normally on the ink layer surface if the polyester film (A) has an ink layer), and then drying to form an adhesive layer without surface adhesion.

[0057] Application of the adhesive of the present invention onto the polyester film (A) may be performed by a previously known method such as the roller coating method, die coating method, gravure method, gravure offset method, or spray painting method, and normally is applied such that the dry film thickness is between approximately 0.3 and 15 μm, and then the film is dried, for instance, at a temperature between 50°C and 180°C in order to remove the solvents of the adhesive layer.

[0058] In Step (2), the polyester film (lamination film for laminating metal plate) with an adhesive layer that was obtained in Step (1) is rolled into a coil. This coil is stored until used for laminating a metal plate.

[0059] In Step (3), the coil of lamination film for laminating a metal plate obtained in Step (2) is uncoiled and laminated onto the metal plate.

[0060] The aforementioned metal plate which is used for laminating may be, for example, hot rolled steel sheet, cold rolled steel sheet, melted zinc plated steel sheet, electrolytic zinc plated steel sheet, iron-zinc alloy plated steel sheet, zinc-aluminum alloy plated steel sheet, nickel-zinc alloy plated steel sheet, nickel- tin alloy plated steel sheet, tin plate, chrome plated steel sheet, aluminum plated steel sheet, tungsten plated steel sheet, nickel plated steel sheet, stainless steel, tin-free steel, aluminum sheet, copper sheet, titanium sheet, and other metal sheet materials; chemically treated metal sheet made by chemically treating these metal sheets such as with a phosphate treatment, chromate treatment, or a compound oxide film treatment; or painted metal sheet such as a primer painted metal sheet with a primer layer such as a white coat formed on the surface of the aforementioned metal sheet materials or chemically treated metal sheet.

Furthermore, with the present invention, "metal plate" may be a flat sheet like metal plate such as the aforementioned metal sheet materials, chemically treated metal sheet, or primer painted metal sheet, but, for instance, also includes processed metal sheet which has been processed to form, for instance, a can body, or the like.

[0061] The conditions for overlaying the aforementioned metal plate onto the adhesive layer surface of the lamination film for laminating metal plate is not particularly restricted so long as the lamination film for laminating a metal plate is not degraded, the PET film and the metal plate are sufficiently bonded, and a PET laminate metal plate with good appearance is obtained. One example of the overlaying conditions which can be suggested is a method where the temperature of the metal plate is increased to be approximately 120°C to 200°C when thermocompressed using a method which uses a heating roller or a method where the metal plate is a preheated, and then the metal plate and the lamination film for laminating metal plate are thermocompressed for a short period of time (normally less than approximately 2 seconds) and laminated. If a flat metal plate is used, the lamination film for laminating metal plate can be thermally laminated onto one or both sides of the flat metal plate.

[0062] The adhesive layer of the laminated metal plate obtained as described above is hardened by electron beam irradiation, but this electron beam irradiation may be performed either before the flat PET laminated metal plate is formed or after forming. Of course, if the PET laminated metal plate is in the desired shape, the PET laminated metal plate which has been electron beam irradiated will not require forming.

[0063] The accelerator of the electron beam generating source used to irradiate the electron beam may be a Cockcroft accelerator, Cockcroft-Walton accelerator, Van de Graaff accelerator, resonance transformer, transformer, insulated core transformer, Dynamitron, linear fillament, area beam accelerator or high frequency accelerator, or the like. The electron beam energy required to harden the electron beam-hardening adhesive layer is between 100 KeV and 300 KeV, and preferably within a range between 150 KeV and 200 KeV. The irradiation beam intensity is typically between 0.2 Mrad and 15 Mrad, but between 1 Mrad and 5 Mrad is particularly preferable from the viewpoint of the hardness of the adhesive layer and the mechanical strength.

The irradiation time for the electron beam is normally less than approximately 1 second, approximately 1/50th of the time required for thermal hardening.

[0064] The PET laminated metal plate of the present invention is suitably used for metal cans such as cans for beverages, cans for food, cans for miscellaneous, and 5 gallon cans as well as for caps and other metal lid applications, and furthermore, may also be used for thermos bottles, or the outside of home appliances such as refrigerators surfaces.

[0065] PREFFERED EMBODIMENTS

The present invention will be described in further detail using preferred embodiments.

[0066] Hereinafter, both "parts" and "%" are based on a weight standard.

[0067] Manufacture of Polyester Resin (a)

Manufacturing Example 1

0.3 mol of terephthalic acid, 0.55 mol of isophthalic acid, 0.15 mol of sebacic acid, 0.25 mol of ethylene glycol, 0.2 mol of 1,4-butanediol, 0.33 mol of neopentyl glycol, 0.2 mol of 1,4-dimethylol cyclohexane, 0.02 moles of trimethylol propane, and a suitable amount of polymeric condensation catalyst were added to and heated in an autoclave to perform an esterification reaction, and a polyester prepolymer was obtained after a stoichiometric amount of condensation water was removed. 0.25 mol of maleic anhydride was then added to 1 kg of the polyester prepolymer thus obtained, and heated and mixed to perform additional reactions before cooling and adding a solvent blend (toluene/methylethyl ketone = 50/50 (weight ratio)) to obtain a polyester resin (a-1) with 40% solid content.

[0068]

Manufacturing Example 2 through 13

Various polyester resins were obtained in similar manner to Manufacturing Example 1, except that the polybasic acid component, polyhydric alcohol component and an additional acid component were as shown in the following Table 1. Manufacturing Examples 7 through 13 are manufacturing methods of polyester resins for comparison. In Table 1, the formulation amount of acid component and alcohol component are molar quantities, and the formulation amount of the additional acid component is shown as a molar quantity for 1 kg of polyester prepolymer obtained by the esterification of the acid component and the alcohol component.

[0069] The arithmetic mean molecular weight (Mn) weighted mean molecular weight (Mw), Mw/Mn ratio, glass transition temperature (°C) hydroxyl value (KOH mg/g), and acid value (KOH mg/g) for each of the polyester resins obtained in the aforementioned Manufacturing Examples 1 through 13 are shown below in Table 1.

[0070] Table 1

		Manufacturing Examples												
		1	2	3	4	5	6	7	8	9	10	11	12	13
Acid Component (moles)	Terephthalic acid	0.3	0.3	0.3	0.3	0.25	0.3	0.3	0.3	0.3	0.3	0.35	0.25	0.3
	Isophthalic acid	0.55	0.55	0.55	0.55	0.5	0.55	0.55	0.55	0.55	0.55	0.65	0.50	0.55
	Sebacic acid	0.15	0.15	0.15	0.15	0.25	0.15	0.15	0.15	0.15	0.15	--	0.25	0.15
Alcohol Component (moles)	EG	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
	1,4-BG	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.2
	NPG	0.33	0.33	0.31	0.31	0.33	0.33	0.35	0.33	0.34	0.35	0.33	0.33	0.29
	CHDM	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2
	TMP	0.02	0.02	0.04	0.04	0.02	0.02	--	0.02	0.01	–	0.02	0.02	0.06
Additional Acid Component	Maleic anhydride	0.25			0.25	0.25		0.08		0.33	0.08	0.25	0.25	0.08
	Trimellitic anhydride			0.15			0.08							
	Succinic anhydride		0.25											
(mol/kg prepolymer)														
Properties of Polyester Resin	Arithmetic mean molecular weight	20,000	19,000	15,000	17,000	19,000	17,000	20,000	17,000	17,000	9000	18,000	17,000	14,000
	Weighted mean molecular weight	77,000	61,000	66,000	104,000	73,000	56,000	40,000	52,000	59,000	20,000	63,000	61,200	84,000
	(Mw/Mn) ratio	3.8	3.2	4.4	6.1	3.8	3.3	2.0	3.1	3.5	2.2	3.5	3.6	6.0
	Glass transition temperature (°C)	39	39	38	38	23	39	40	39	40	34	65	18	38
	Hydroxyl value KOH mg/g	6	7	9	11	6	11	5	19	1	5	6	5	23
	Acid value KOH mg/g	16	16	20	15	17	9	5	0.6	22	7	6	6	4
Name of Polyester Resin		a-1	a-2	a-3	a-4	a-5	a-6	a-7	a-8	a-9	a-10	a-11	a-12	a-13

[0071] Manufacture of Electron Beam-Hardening Adhesive

Embodiment 1

180 parts of titanium white, 20 parts of body pigment (clay), and an appropriate amount of a solvent blend (toluene/methylethyl ketone = 50/50 (weight ratio)) were added and dispersed in 100 weight parts of a polyester resin (a-1) solution with a solid content of 40% obtained in Manufacturing Example 1, this dispersion was then blended with 137.5 parts of the aforementioned polyester resin with a solids content of 40% (55 parts based on solid content), 5 parts of "Aronix M-315" (product of Toagosei Co. Ltd., polyester containing polymeric unsaturated groups, polymeric unsaturated double bond concentration approximately 7.0 mol/kg, arithmetic mean molecular weight approximately 420, essentially no hydroxyl value), 25 parts (20 parts based on solid content) of "Duranate TPA-B80X" (product of Asahi Kasei, hexamethylene diisocyanate type blocked polyisocyanate compound, solid content 80%), and 3 parts of "Duranate TPA100" (product of Asahi Kasei, hexamethylene diisocyanate polyisocyanate compound) and methylethyl ketone to make an electron beam-hardening adhesive with a solid content of 50%.

[0072] Embodiments 2 ~ 12 and Comparative Examples 1 ~ 11

Various electron beam-hardening adhesives were obtained by the same manner as Embodiment 1, except that the formulation composition was as shown in the following Table 2. The formulation amounts of each of the components in Table 2 are expressed in solid weight units. In Table 2, the (Notes) have the following meanings.

[0073] (*1) EB-450: Product of UCB S. A. Specialty Chemicals, polyester oligomer with polymeric unsaturated groups, polymeric unsaturated double bond concentration of approximately 4 mol/kg, arithmetic mean molecular weight of approximately 1500, and a hydroxyl value of 50 KOH mg/g.

[0074] (*2) Aronix M-8100: Product of Toagosei Co., Ltd., polyester oligomer with polymeric unsaturated groups, polymeric unsaturated double bond concentration of approximately 6.7 mol/kg, arithmetic mean molecular weight of approximately 600, and essentially no hydroxyl groups.

[0075] Manufacture of PET Laminated Metal Plate

Each of the electron beam-hardening adhesives obtained from Embodiments 1 through 12 and Comparative Examples 1 through 11 were applied to a dried film thickness of approximately 3 µm using gravure application onto the corona discharge treated surface of ester film E-5100 (polyester film with a film thickness of 12 µm) (corona discharge treated on one side) produced by Toyobo Co. Ltd. The film was then passed through a drying oven at 100°C for 10 seconds to evaporate off the solvent component. The polyester film with adhesive applied was tested for adhesive layer surface tackiness, and blocking resistance based on the following test methods. These test results are shown in the following Table II.

[0076] This polyester film with adhesive applied was thermally laminated onto Canlite (product of Nippon Steel Corp. which is a 0.19 mm thick tin plate, at a roller temperature of 180°C and a roller pressure of 5.0 kg/cm2. Then, an electron beam was irradiated through the polyester film of the laminated metal plate at a current of 50 mA, an intensity of 4 Mrad, and an acceleration voltage of 270 KeV using an electron beam accelerator to harden the adhesive layer in order to obtain each of the PET laminated metal plates.

[0077] The PET laminated metal plate obtained as shown above was tested for the surface appearance and retort resistance adhesion of the laminated polyester film based on the following test methods. These test results are shown in Table 2.

[0078] Test Items

Tackiness: The adhesive coated surfaces of two adhesive coated polyester films obtained by evaporating off the solvent component (approximately 10 seconds after removing from the drying oven) were overlaid and sufficiently compressed by hand, and then the two films were pulled apart and evaluated for the area of peeling on the side of the two adhesive coated surfaces which had the larger area of peeling of adhesive from the polyester film.

(O): absolutely no peeling was observed on either of the two adhesive coated surfaces.

O: Peeling was observed and the area of peeling on the larger side was less than 10%.

□: The area of peeling of the larger side was 10% or larger but less than 30%.

X: The area of peeling of the larger side was 30% or more.

[0079] Blocking resistance: A surface, formed by corona discharge treating a separate "Ester Film E5100" and then forming a epoxy-polyester overcoat paint film on the treated surface, was overlaid facing the surface of the adhesive on the surface of an adhesive coated polyester film obtained by evaporating the solvent component, a 10 kg/cm^2 pressure was applied, and the film was stored in a room at a temperature of 25°C and a relative humidity of 60%RH for three days. The stored laminated film was cut to a width of 30 mm, and the peeling strength (g/30 mm wide) was measured when the separate PET film was peeled from the dried film surface at an angle of 180 degrees at a peel speed of 500 mm/minute, and an evaluation was performed according to the following criteria.

(O): Peel strength is less than 10 g/30 mm wide

O: Peel strength is 10 g/30 mm wide or higher but less than 20 g/30 mm wide

□: Peel strength is 20 g/30 mm wide or higher but less than 50 g/30 mm wide

X: Peel strength is 50 g/30 mm wide or higher

[0080] Film surface appearance: Using the same laminate prepared for the aforementioned blocking resistance test, a different PET film which had been placed on the dried coated surface was peeled from the laminate film after storage for two days and four days at room temperature, and a 0.2 mm thick tin plate was laminated onto the dried film surface obtained at a lamination temperature of 160°C, linear pressure of 50 kg, and speed of 200 m/minute, and the appearance of the PET laminate surface of the PET laminated metal plate obtained was evaluated according to the following criteria.

(O): No problems were observed in the PET laminate surface

O: Slight orange peel surface observed on the PET laminate surface

□: Moderate orange peel surface observed on the PET laminate surface

X: Severe orange peel surface observed on the PET laminate surface.

[0081] Laminate strength: the PET laminate metal plate prepared for the aforementioned appearance test of the film surface was cut to a 15 mm width (laminate storage period 24 hours), and a peel test was performed between the PET film and the tin plate, and the difficulty of peeling was evaluated according to the following criteria.

(O): PET film did not peel at all

O: A part of the PET film peeled, but the PET film broke before the peel length reached 5 mm

□: A part of the PET film peeled, but the PET film broke when the peel length was 5 mm or longer, but less than 20 mm

X: The PET film peeled and the PET film peeled completely off or broke at a peel length of 20 mm or longer.

[0082] Retort resistance adhesion in the formed region: The PET laminate metal plate prepared for the aforementioned film surface appearance test was pressed with the tin plate side facing up in a 200 Endo forming apparatus (can lid forming machine), the can with lid that was created was subjected to retort processing in steam at 125°C for 30 minutes, and the peeling condition of the PET film was evaluated according to the following criteria.

(O): Absolutely no peeling of the PET film was observed

O: Slight peeling of a part of the PET film in the circumferential region

□: Moderate peeling of a part of the PET film in the circumferential region

X: Peeling around the whole circumferential region of the PET film

[0083] Table 2

			Comparative Examples											
			1	2	3	4	5	6	7	8	9	10	11	12
Polyester resin (a)	Type		a-1	a-1	a-1	a-1	a-1	a-1	a-1	a-2	a-3	a-4	a-5	a-6
	Amount (parts)		95	90	80	95	90	90	90	90	90	90	90	90
Polymeric unsaturated oligomer (b)	Aronix M-315		5	10	20		5		10	10	10	10	10	10
	EB-450 (*1)					5	5							
	Aronix M-8100 (*2)							10						
Blocked polyisocyanate			20	10	--	5	5	10	15	5	5	5	5	5
Unblocked polyisocyanate			3	5	7	5	5	5	5	5	5	5	5	5
Titanium white			180	180	180	180	180	180	180	180	180	180	180	180
Body pigment			20	20	20	20	20	20	20	20	20	20	20	20
Test Results	Adhesion		(O)	(O)	O	(O)	(O)	O	O	(O)	(O)	(O)	(O)	(O)
	Blocking resistance		(O)	(O)	O	(O)	(O)	O	O	(O)	O	(O)	O	(O)
	Appearance of film surface	2 days after application	O	(O)	(O)	(O)	(O)	(O)	O	(O)	(O)	(O)	O	(O)
		4 days after application	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)
	Laminate strength		O	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)
	Retort adhesion in formed region	2 days after application	(O)	(O)	(O)	O	O	(O)	(O)	(O)	(O)	(O)	(O)	(O)
		4 days after application	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)	(O)

[0084] Table 3

Table 2 (Continued)

			1	2	3	4	5	6	7	8	9	10	11
Polyester resin (a)	Type		a-1	a-1	a-1	a-2	a-7	a-8	a-9	a-10	a-11	a-12	a-13
	Amount (parts)		98	75	90	100	90	90	90	90	90	90	90
Polymeric unsaturated oligomer (b)	Aronix M-315		2	25	10		10	10	10	10	10	10	10
	EB-450 (*1)												
	Aronix M-8100 (*2)												
Blocked polyisocyanate			10	--	10	5	5	5	5	5	5	5	5
Unblocked polyisocyanate			5	3	12	5	5	5	5	5	5	5	5
Titanium white			180	180	180	180	180	180	180	180	180	180	180
Body pigment			20	20	20	20	20	20	20	20	20	20	20
Test Results	Adhesion		(O)	□	□	(O)	X	O	X	X	O	□	O
	Blocking resistance		(O)	□	X	(O)	X	(O)	(O)	X	(O)	X	(O)
	Appearance of film surface	2 days after application	(O)	□	(O)	(O)	X	□	□	X	(O)	□	(O)
		4 days after application	(O)	O	(O)	(O)	□	O	□	X	(O)	O	(O)
	Laminate strength		□	(O)	(O)	X	O	O	O	□	□	O	O
	Retort adhesion in formed region	2 days after application	X	□	(O)	□	X	□	□	X	X	O	X
		4 days after application	□	□	(O)	□	□	□	□	X	X	(O)	X

[0085] EFFECT OF THE INVENTION

By using the adhesive of the present invention, an excellent adhesive layer can be formed which can be used for a long period of time, and the polyester film which forms the adhesive layer has favorable blocking resistance toward the adhesive layer, and the adhesion to the metal plate is excellent.

[0086] Furthermore, the PET laminate metal plate made by laminating a polyester film formed with this adhesive layer will have excellent appearance on the PET film surface, as well as excellent forming properties and retort resistance, and the like.

[0087] The PET laminate metal plate which uses the adhesive of the present invention can be favorably used for can applications such as the inside and outside surface of the can.